

~~CONFIDENTIAL~~

070 2095

National Aeronautics and Space Administration
Contract No. NASw-6

Publication No. 160

THE EFFECT OF METAL ADDITIVES
ON THE COMBUSTION AND
PERFORMANCE OF SOLID PROPELLANTS



uke
Peter L. Nichols *jr.*

~~CONFIDENTIAL~~
~~UNCLASSIFIED~~
~~CONFIDENTIAL~~
~~CONFIDENTIAL~~

COPY NO.
W 0 H _____
L _____ C _____
E _____ M _____
A _____ S _____

Copy No. 15
pp. ii, iii, 1-35

CLASSIFICATION CHANGE

To UNCLASSIFIED
By authority of GDS - Eys/652
Changed by O. Stuebelman 12/31/72
Classified by _____ on _____, NASA
Scientific and Technical Information Facility

JET PROPULSION LABORATORY
California Institute of Technology
Pasadena 3, California

APR 17 '59

~~CONFIDENTIAL~~

CONTENTS

	Page
I. Introduction	1
II. Experimental Techniques	2
A. Strand Data	3
B. Closed Bomb Tests	3
C. Motor Techniques	5
D. Photographic Studies	6
E. Chemical Analysis	12
III. Combustion Characteristics	12
A. Burning Rate - Pressure Dependence	13
B. Temperature Sensitivity.	16
C. Wires versus Powders	18
D. Unstable Burning	20
E. Ignitibility, Shock Sensitivity, and Detonability	21
IV. Motor Performance	22
A. Propellants Containing Aluminum	22
B. Miscellaneous Results	23
C. Problem Areas	24
V. Summary	25

CONTENTS (Cont'd)

	Page
Tables	27
References	30
Figures	32

TABLES

I. Ease of Particle Ignition	27
II. Ignitibility Limit	27
III. Degree of Boron Combustion in Polyurethane Propellants	28
IV. Effect of Tube Length on Extent of Boron Combustion	29
V. Burning Rate Data on Aluminized Propellant	29

FIGURES

1. Aluminized Propellant Burning
2. Metal Particles Burning in Pilot Flame
3. Burning Time vs Diameter for Mg and Ti Particles
4. Burning of Propellant Containing Mg-Al (50 - 50 wt %) Alloy
5. Generalized Burning-Rate Curves

~~CONFIDENTIAL~~

THE EFFECT OF METAL ADDITIVES ON THE COMBUSTION AND PERFORMANCE OF SOLID PROPELLANTS

Peter L. Nichols, Jr.

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

ABSTRACT

A general review of the effect of metal additives on the combustion characteristics of solid propellants is given. Metal additives were initially introduced to increase propellant specific impulse and density. It was demonstrated experimentally that metal additives can also be used to suppress unstable burning in rocket motors and to produce significant modification in propellant ballistic properties. Studies have also revealed that complexities in the combustion of metal additives in solid propellants have an important influence on experimentally delivered specific impulse. Available data relating to all the above-mentioned effects are analyzed and, wherever possible, existing theory is employed in an attempt to correlate and explain results obtained thus far.

I. INTRODUCTION

The advent of intercontinental ballistic missiles and space exploration has placed considerable emphasis on the development of high-performance solid propellants. In order to maintain simplicity in rocket-motor design, to keep inert-parts weight to a minimum, and to optimize powerplant performance, it proved necessary that the high performance propellant satisfy simultaneously a complex set of ballistic and mechanical property requirements.

A natural step in increasing the performance of conventional solid propellants capable of satisfying these requirements, therefore, was the addition of metal powders which would provide increased specific impulse by virtue of their large heats of oxidation. Increased density resulting from the replacement of the organic fuel with the metal fuel was also important in increasing over-all performance. Early investigations which tended to give more emphasis to the ballistic modifications resulting from the addition of metal powders have now been extended to include the factors affecting the performance of solid propellants containing appreciable quantities of metal

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

constituents. The discovery that relatively small quantities of metals reduce unstable burning in solid-rocket motors has also emphasized the importance of these additives in solid-rocket motor development.

In choosing subject matter for a survey of the effect of metal additives on the combustion of solid propellants, it was decided to confine attention mostly to propellant systems employing ammonium perchlorate as oxidant and in which the resin binders vary from materials containing little or no oxygen, such as polybutadiene copolymers, to the highly oxygenated double-base propellant materials. The decision was based on the following considerations: (1) A large quantity of data exists on these systems, (2) primary emphasis is being placed on these systems at present for the development of large solid rocket engines, and (3) conclusions drawn from the investigation of these systems might be applicable to, or at least serve as a standard for comparison with, other systems which might assume importance in the future.

The term "metal additive" in this paper applies to metals in the form of powders and wires, and to metal hydrides and alloys of the metals in powdered form. The term additive is used in a general sense and covers the case in which the additive is actually an important fraction of the fuel employed. A weight fraction range of 2 - 25% of the propellant composition covers most cases considered. Other compounds of the metals will not be included, although many metallic compounds have a profound influence on the ballistic properties of propellants, particularly when applied to double-base propellants. The well-known phenomenon of plateau and mesa production in double-base propellants covers too wide an area to be adequately covered in the present paper. The extent to which such desirable characteristics are altered by the introduction of metal additives, as defined herein, will be treated briefly, however.

II. EXPERIMENTAL TECHNIQUES

Recent advances in the development of large solid-rocket engines, coupled with the inherent simplicity and reliability of these powerplants, have prompted a large increase in the research and development efforts on high-performance solid propellants. This increased emphasis has created a substantial increase in the number of organizations and personnel participating in solid-propellant R and D, and a greater need than ever for the proper recording, interpretation, and dissemination of data from the solid propellant R and D programs underway. Since the addition of metal additives provides an important path which might lead to significantly greater experimental

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

performance than that which now exists, and since the number of alternate paths at present are few, it will be important to examine the experimental techniques now being used to collect data on ballistic properties and performance of solid propellants. The discussion is intended to point out the most important virtues, limitations, and pitfalls in applying available techniques to metallized systems. With such a background, it will be easier to assess the value of the data to be presented and the conclusions drawn from them.

A. Strand data

The simplest and most widely used technique for obtaining preliminary ballistic data is the well-known Crawford bomb. Experience has shown that in most cases such data are useful and reasonably reliable; however, there are many instances in which strand data yield pressure-burning rate relationships which are purely characteristic of the test itself and not a property of the propellant fired in motors. Therefore, all strand data must receive final confirmation in motor firings. It should also be emphasized that good strand-data gathering requires careful technique. The length of strand, method of restriction, tendency of the strand to burn with a large cone angle, physical factors involved in the combustion of the propellant, geometry of the propellant strand, and preparation of the propellant charge and strand influence the final result. There have been many instances of formation of false plateaus and mesas, as well as establishment of fictitious combustion limits with strand data.

Despite the recognized limitations in strand data, this technique will continue to be of great value in preliminary investigations. Also, it should be mentioned that, as a result of specific effects of the metal-powder addition, the kind of data obtained by the strand-data technique is less susceptible to error than data from most other techniques for the evaluation of propellants.

B. Closed-bomb tests

The use of the closed bomb to obtain heats of combustion of propellant materials is well understood and requires no consideration at this time. The determination of heats of explosion of metallized propellant systems is not so well understood, and there is a tendency to attempt to interpret data of this type in terms of combustion efficiency. For example, Aerojet reports (Ref. 1) disclose attempts to determine from heat-of-explosion data the effect of particle size on efficiency of combustion of aluminum in certain polyurethane propellant compositions. Also, the effect on combustion efficiency of

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

of replacing a small amount of the aluminum with other metals was studied in this manner. In each case, the changes in heat of explosion were only a few per cent, and there is reasonable doubt concerning the conclusions reached. The conditions in the bomb are quite different from those obtained in a rocket motor. The value of heat-of-explosion data in reflecting changes in combustion efficiency is small even under the best circumstances.

Use of the closed bomb to determine specific impulse is another case in which the results obtained on metallized systems are of questionable value. The confusion arising from these indirect techniques often overshadows the value of results which do reflect real differences among propellant compositions.

The usual technique employed in obtaining impulse data with the closed bomb is as follows (Ref. 2): A small sample of propellant is ignited in a vessel that is either evacuated, or slightly pressurized with an inert gas. The pressure vs time is recorded, and from the decreasing part of the pressure-time curve an extrapolation is made to obtain a pressure at zero time. Among various organizations using the technique, different extrapolation procedures have been contrived. Since the decreasing part of the pressure-time curve is connected with heat transfer, and since the heat-transfer characteristics of propellant gases with condensibles differ markedly from those containing non-condensibles, the extrapolation procedure could cause considerable variations in reported results. An appropriate equation of state for the product gases, recognition that impulse is proportional to $\sqrt{nRT_c}$ and realization that C_p/C_v does not vary markedly with most propellant compositions, serve as the bases for obtaining specific impulse from closed-bomb pressure-time data. It is possible to perform a direct calculation for the specific impulse by calculating C_p/C_v for the product gases. A better method, however, is to determine the specific impulse relative to a standard composition.

In examining specific-impulse values from closed-bomb tests, it is important to keep in mind that the results tend to be high rather than low as compared to those obtained in motor tests. The result is primarily due to the fact that more complete combustion is encountered in the bomb. An erroneous high result, however, can be quite unfortunate if the error is not recognized in time. Former enthusiasm concerning the potentialities of boron hydrides in increasing performance is well-remembered in this respect. A reasonably critical attitude toward specific-impulse data from closed bombs is recommended, therefore.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

C. Motor techniques

The final and most important test of propellant performance is, of course, the actual firing in a rocket motor under the chosen operating conditions. As a matter of fact, measurements during flight most often yield the best possible means for determining the reproducibility of propellant performance. Nevertheless, in the development of new propellants, static testing is essential, and it is important to know the extent to which static tests yield reliable data.

Experience with non-metallized propellants has shown that a static-test motor should contain a minimum of 1-2 lb of propellant if useful data are to be obtained. Even with this size motor, heat losses are usually significant, and C^* data are more accurately obtained than thrust data. Motors containing 10-30 lb of propellant yield greatly improved data, and in this size range reasonably accurate thrust data can be obtained, e.g., 1-2% variations in specific impulse calculated from the thrust measurement.

The introduction of metal powders has limited the utility of small motor tests considerably. The measurement of C^* in motors with small diameter nozzles (of the order of tenths of an inch) is complicated by the coating on the inside nozzle surface, with a corresponding change in effective throat diameter. Also, combustion of the metal powders in small motors is incomplete. An effect analogous to the L^* effect in liquid-rocket motors must be considered. No general rule can be given at this time with regard to minimum motor size in terms of L^* , particle residence time, or other parameter. It is worthwhile to observe, however, that Aerojet data to be discussed in Sec. IV-A suggest that motors containing 90 lb or more of propellant are required for obtaining performance data which could be applied with confidence to rocket motors of arbitrary size. It should be emphasized that the primary difficulty with metallized systems lies in obtaining accurate C^* and thrust data and not in obtaining ballistic data such as burning rates, pressure exponents and temperature sensitivities.

Before closing this discussion of motor techniques, a description of results obtained with the JPL flywheel tester (described in Ref. 3) will be of value in giving a more quantitative idea of the limitations of small-motor tests in measuring performance of metallized propellants. The instrument was claimed to be capable of measuring impulse to an accuracy of $\pm 0.3\%$ and a reproducibility of $\pm 0.1\%$. The standard deviation for a group of tests using a polyurethane propellant of $I_{sp} = 235$ sec was found to be 0.8%. When

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

metallized propellants were tested, however, the following results were typical. A polyurethane propellant JPL X550, containing 15% aluminum, gave a measured I_{sp} of 238.6 sec approximately 91% of theory. Closely similar Aerojet propellants have delivered up to 96% of theory in large motors. The Naval Ordnance Test Station (NOTS) high-energy nitrasol H3515 propellant delivered 239 sec (~90% theory). For the same propellant, NOTS reports 255 sec delivered in 35-lb motors. A high-energy JPL propellant of the X560 type delivered 243 sec with the flywheel tester compared with an expected 250-260 sec in large-motor firings.

D. Photographic studies

The use of photography in studying the combustion of metal powders is proving of considerable value in revealing many significant features of the combustion process. A summary of results of a program being conducted at the Jet Propulsion Laboratory will be given to illustrate the kind of information being obtained in this manner.

It is well known that most conventional propellants burn completely in a narrow zone close to the burning surface. In composite propellants employing ammonium perchlorate as oxidant this zone is of the order of a millimeter thick. In Fig. 1, a significant feature of metallized propellant burning is revealed, viz., the metal particles are carried along with the combustion gas stream for considerable distances before they burn to completion. There are several implications resulting from this observation, such as (1) a certain fraction of unburned metal might be ejected from the rocket motor, thus affecting motor performance, (2) the entire heat-release pattern of the combustion system may depend on the kinetics of the combustion of the metal powder and, in turn, the ballistic properties of the propellant may be affected, and (3) a more detailed study of the combustion of the powder would reveal the factors necessary for obtaining maximum combustion efficiency.

Much preliminary information was obtained by burning metal powders in a gas-air pilot flame into which the metal particles were axially injected in the center of the flame, using oxygen as a carrier gas. The burning particles were photographed with a 4 x 5-in. still camera using color film (Anscochrome, tungsten) especially processed to give a higher light speed (ASA 128 instead of ASA 32). A shutter speed of 1/50 sec was used. The burning particles appeared as streaks, as illustrated in Figs. 2a through d. The length of the streak, divided

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

by the oxygen velocity, was used as a measure of burning time. The pilot flame was adjusted to the minimum size necessary to give ignition.

Several objections can be raised to quantitative interpretations from experiments of this kind, e.g., (1) the particle velocity is not strictly constant, (2) the pilot flame has a complicated structure leading to poorly defined ignition conditions for the particle in question, (3) heating of the particle varies in each experiment such as to obscure the contribution of the flame in heating the particle, as compared with self-heating.

In spite of the complexities in interpreting results, the experiments have brought out large qualitative differences in burning rate and mechanism; the most important of these will be discussed. The following substances¹ have been considered: Be, B, C (graphite), Mg, Al, Si, S, Ti, Fe, Co, Zn, Zr, Sb, LiH, MgH₂, LiAlH₄, CaH₂, TiH₂, ZrH₂, TiC, ZrN, Al-Mg alloys, AlB₂, Al-Ti (1 to 3 mol ratio), Al-Ti (1 to 1 mol ratio), Al (77 wt %) - Ti (23 wt %), Al (94 wt %) - Ti (6 wt %), and TiB₂.

Dr. Derck Gordon, who has been conducting this program at the Jet Propulsion Laboratory, has been able to draw a number of interesting qualitative conclusions with regard to the burning of metal powders. These conclusions, which are listed below, illustrate the kind of information which can be gained by this technique and, at the same time, call attention to the complexities of metal powder combustion.

1. Burning rate and ignitibility of a given metal increase with decreasing particle size.
2. Above a certain particle size, depending on conditions, ignition will not occur in the torch. This is because the particle acts as a heat sink which rapidly removes the heat transferred from the surroundings and the heat of reaction from the reaction zone, quenching the reaction or preventing it from starting.

¹Phase diagrams were used as guides in selecting alloys. Particles were classified using standard screens in the following groups: < 35 mesh, 35 - 60 mesh, 60 - 100 mesh, 100 - 150 mesh, 150 - 325 mesh, and > 325 mesh.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

3. Burning rate and burning mechanism are not "structure sensitive" as are the mechanical properties of metal. Small changes in composition make only small changes in burning rate in general. Hence, in investigating an alloy system, it is not necessary to investigate many samples of slightly different composition but only samples representing the major phases. The state of phase equilibrium is also not important. Small additions of alloying elements may be added to produce secondary desirable properties without greatly altering the burning rate in general.
4. Pure metal particles appear to burn according to one of the following mechanisms, depending on composition, particle size, and ignition conditions.
 - a. Volatile metal. The metal vaporizes at the surface of the particle and reacts with oxygen in a homogeneous gas-phase reaction. The oxide, if condensable, condenses outside the reaction zone.
 - b. Nonvolatile metal, volatile oxide. Oxygen reacts with solid or liquid metal at particle surface, forming volatile oxide. No oxide layer is formed to impede reaction. Heat of vaporization extracted by oxide may, under certain conditions, cool the particle below ignition temperature.
 - c. Nonvolatile metal, nonvolatile insoluble oxide. Oxygen reacts with solid or liquid metal either after oxygen has diffused through the oxide layer or after the metal has diffused out through the solid or liquid oxide layer. In either case, the ever-thickening oxide layer more or less impedes the reaction, whether "protective" or not.
 - d. Nonvolatile metal, soluble oxide. Oxygen reacts with solid or liquid metal at the particle surface and then diffuses into the particle away from surface because of an inherent solubility in the metal. Hence, accumulation of oxide impedes reaction to a lesser extent than if an oxide layer built up at the particle surface.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

- e. Fragmentation. In addition to one of the above mechanisms, a mechanism involving ultimate fracture of the particle may be superimposed. At one time it was believed that the fracture mechanism was connected with crystal structure, particularly with the hexagonal crystal structure of the metals Mg, Ti and Zr, in which it was observed. This no longer appears probable since it does not occur with beryllium, which is also hexagonal. Rather, it is probable that the fracture is a "catastrophe" resulting from internal thermal stresses set up when the oxidation takes place at an ever-increasing rate, i. e., as a burning magnesium particle grows smaller, reducing the heat sink and raising the entire particle to its boiling point, or, as a burning titanium particle grows hotter, increasing the reactivity of oxygen with the metal, making the rate of heat production increase exponentially until the boiling point of the metal is reached.
5. To which of the above classes a particular metal belongs depends to some extent on conditions. For example, under conditions prevailing in the particle-burning torch in which ignition temperatures in the range of 500 to 1500° C prevail, Mg (-325 mesh) is in class "a" (volatile metal), whereas Al (-325 mesh) is in class "c" (nonvolatile metal, nonvolatile insoluble oxide). However, under conditions of higher temperature, which occur when the concentration of metal in the oxygen streams is greatly increased, the combined radiation of many incandescent aluminum particles raises the temperature of the surroundings sufficiently such that, at a critical point, the aluminum particles vaporize, causing the character of the "flame" to change very suddenly from a mass of incandescent streamers to a tiny, brilliant spot of light. The substances investigated are classified below according to burning mechanism for ignition conditions prevailing in the particle-burning torch for low particle concentration. This classification applies also for particles burned in a metallized strand, to the extent that tests have been made.
- a. Volatile substance: Mg, Zn, Sn, LiH, MgH₂, CaH₃.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

- b. Nonvolatile substance, volatile oxide: C (graphite), B (amorphous). The boiling point of B_2O_3 is reported to be $1500^\circ C$, so that the burning of boron should not be retarded by an oxide layer. Particles of B which have passed through the pilot flame are found to be coated with an oxide layer. Evidently, the temperature of the pilot flame is not sufficient to vaporize the oxide. The slow-burning character of B may also be due to a high ignition temperature, concomitant with its high melting point ($2040^\circ C$).
 - c. Nonvolatile substance, nonvolatile insoluble oxide: Be, Al, Si, Fe, Co, AlB_2 , TiB_2 , $TiAl_3$.
 - d. Nonvolatile substance, soluble oxide: Ti, TiC, Zr, ZrN, ZrH_2 , TiH_2 , Ti-6 wt % Al. The carbides, nitrides, and hydrides are included in the list since all the listed substances have practically identical burning characteristics--burning particles appear as long streaks, becoming more brilliant as they progress, finally exploding. Clearly, the C, N, and H must be lost during the burning as volatile oxides; however, this process cannot be seen.
 - e. Fragmentation: Mg, Mg-Al alloys above about 10 wt %, Mg, Ti, Zr, TiH_2 , ZrH_2 , TiC, ArN, MgH_2 , CaH_2 , Ti-6 wt % Al. In addition to fracturing, Mg particles of larger size, above about 150 microns, are self-propelled in remarkable spiral and erratically turning trajectories by expulsion of Mg vapor when burning occurs unevenly over the surface.
6. An alloy or compound may burn by a more complex scheme than the above, depending on its composition. If the alloy contains a volatile constituent (H, Mg, Li, Ca), the volatile constituent will distill out of the particle and react with oxygen in a homogeneous gas-phase reaction, leaving the nonvolatile constituent to burn by one of the other mechanisms listed. A good example is $LiAlH_4$, for which it is possible to observe first the burning of hydrogen, then of lithium, and finally of the aluminum residue. The distillation of a volatile component may possibly set up internal stresses

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

which fracture the particle; this is observed in the case of Mg-Al alloys of Mg content greater than about 10 wt % Mg. As noted above, the hydrides and carbides and nitrides of Ti and Zr must burn by a mechanism involving simultaneous solution of oxygen into the titanium lattice and evolution of volatile CO_2 , H_2O , or N_2 .

7. Burning rate. Qualitative differences in burning rate of particles of different substances for approximately the same size distribution were observed with the particle-burning torch despite the uncertainties in interpretation noted above. Past research has been devoted more to observing the qualitative differences of various substances and classifying them according to burning mechanism than to collecting quantitative data on burning rate. The following is a qualitative classification of substances into the classes of "fast burning" and "slow burning," as observed with -325 mesh particles (<44 microns) ignited under minimum conditions in the particle-burning torch. The fast burning particles burn in 0.1 to 1 millisecond; the slow burning particles in 1 to 10 milliseconds or more, and possibly burn only incompletely.

Fast burning: Mg, MgH_2 , Ti, TiH_2 , LiH, CaH_2 , Zr, ZrH_2 , TiC, AlN, Ti-6 wt % Al, Zn, Zr.

Slow burning: Be, B, C, Al, Si, Fe, Co, Sb, LiAlH_4 (Li and H contents burn out rapidly, leaving Al), AlB_2 , TiB_2 , TiAl_3 .

The burning rates of Mg-Al alloys range between that of Mg and that of Al. The slow-burning substances, except Fe, Sb and LiAlH_4 , are more difficult to ignite than the fast-burning substances; also, except for LiAlH_4 , larger particles of fast-burning substances ignited than of slow-burning substances. Additional data are summarized in Tables I and II, and Fig. 3.

The above deductions from powder-burning experiments are not expected to apply in detail to the actual situation which exists in burning metallized solid propellant, but they certainly illustrate many of the complexities in this type of combustion and the need for much additional fundamental studies of metallized solid-propellant flames. It should

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

also be cited that such studies quickly revealed the desirability of investigating Mg-Al alloys in connection with increasing combustion efficiency. It was shown, e. g., that alloys containing relatively small amounts of Mg (5 - 15 wt %) burned more like Mg than Al, and by virtue of this increased combustion rate, such alloys might give higher over-all motor performance. The absence of discrete particle paths in Fig. 4 (as compared with Fig. 1) shows qualitatively the difference in burning rate of Al and Mg-Al alloy. The studies are also in accordance with the observations of rocket-motor firings, which showed that elemental boron gives relatively low combustion efficiency compared with aluminum. Furthermore, the particle-size effects are all in accordance with data from rocket-motor firings. The data also suggest that Be might not yield a sufficiently high performance in propellants to overcome the disadvantage of its high toxicity. The results do not allow a firm conclusion on this point, but they suggest the need for further investigation.

E. Chemical analysis of combustion products

In cases where metals are encountered which give very low combustion efficiency, chemical analysis is valuable in ascertaining the degree of combustion of a metal under various circumstances. Difficulty in burning boron in polyurethane-ammonium perchlorate propellants was demonstrated in this manner². Propellants containing 5 to 10% amorphous boron were burned in a silica chamber and all the products of combustion were trapped and absorbed in water. Analyses of the combustion products burned in a silica tube 0.68 in. I. D. and 3.25 in. in length as shown in Table III. Experiments were also conducted in which the tube length was varied, as shown in Table IV. The small variation in extent of combustion suggested the possibility that the boron particles were coated, and extinguished by the formation of oxide coating. Microscopic examination of the products substantiated this hypothesis. Rocket-motor firings also gave results qualitatively in agreement with the coating hypothesis.

III. COMBUSTION CHARACTERISTICS

An important aspect of the addition of metal additives, whether the primary purpose of the additive be for ballistic modification or performance increase, is that of the compatibility of the additive in the sense of chemical stability of the resulting composition. Aluminum,

²Experiments devised and conducted by Dr. R. F. Muraca.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

for example, has been widely used in many propellant compositions for performance increase; however, up to the present, its use in polysulfide-ammonium perchlorate types is limited in the sense that compositions containing more than 8 wt % produce excessive gasification during cure. Also, magnesium is reactive with most available propellant compositions and must be surface-coated with oxide before use. Obviously, many other metallic additives might prove too active chemically to allow direct addition to the propellant composition. In these cases, it will be necessary to devise methods of providing protective coatings for the additives. One promising technique for vapor deposition of stable metallic coatings on the additives, recently introduced by Dr. R. F. Muraca of this Laboratory, is of interest in this connection. One example of such a coating applied to a specific propellant ingredient produced an unexpected result which emphasized the need for additional understanding of propellant combustion. It was known, for example, that ammonium dichromate generally decreases pressure exponents in ammonium nitrate propellants. A certain ammonium nitrate propellant composition under investigation at the Jet Propulsion Laboratory³ decomposed readily when ammonium dichromate was added. The dichromate, therefore, was coated with magnesium, and the coated salt was added with the production of a reasonably stable propellant composition. The resulting propellant, however, did not have a lower pressure exponent (compared with the uncatalyzed composition) as a result of the dichromate addition.

The coating of oxidants with metals is one of three basic methods which are being used for metallizing propellant compositions. The addition of metal additives in powdered form is another, and the third is the introduction of metals in the form of wires, both oriented and non-oriented. There is not enough information existing on the effect of metal-coated particles on combustion characteristics to treat this subject at the present time. Most qualitative observations resulting from the Jet Propulsion Laboratory program merely suggest that new and interesting effects are to be expected. The addition of wires is a special subject in itself and will only be given brief treatment. Main emphasis will be placed on the addition of metal additives in powdered form.

A. Burning rate-pressure dependence

In order to discuss the burning rate characteristic of metallized propellants, it will be profitable first to review the general

³Work performed by J. Ingham.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

characteristics of combustion of the corresponding unmetallized propellants and then to note the effect of metal addition.

1. Composite propellants. In general composite propellants burn in a manner largely controlled by the oxidant but modified to a significant extent, nevertheless, by the nature of the resin binder. For example, the general level of burning rates of composites containing KClO_4 , NH_4ClO_4 , and NH_4NO_3 is in the order $\text{KClO}_4 > \text{NH}_4\text{ClO}_4 > \text{NH}_4\text{NO}_3$, when compositions of comparable flame temperature are compared (Ref. 4). Note that the per cent of available oxygen is of the same order. Given any of the three oxidants, varying the resin binder in order of decreasing oxygen content does not cause corresponding change in burning rate when compared at the same flame temperature. An exception exists in the case of nitrate compounds which are thermally sensitive, particularly where there is sufficient oxygen to propagate self-combustion. By means of varying the resin binder and by the use of decomposition catalysts which have specific effects according to the oxidant,⁴ it is possible to have a ten- to twenty-fold range of burning rates approximately for each class. Particle size of the oxidant affects the burning rate of ammonium-perchlorate propellants significantly but does not affect that of ammonium-nitrate propellants. This comparison, however, is somewhat obscured by the difficulty of obtaining finely divided ammonium nitrate in propellant compositions.

The pressure exponents of composite propellants are also essentially characteristic of the oxidant. Compositions with $n \leq 0.3$ in the range of 500 - 1000 psi are usually easily achieved with ammonium perchlorate propellants; however, KClO_4 and NH_4NO_3 propellants usually have rather high pressure exponents. An n between 0.3 and 0.4 can often be achieved with NH_4NO_3 propellants with a good burning-rate catalyst such as ammonium dichromate. On the other hand, plateaus

⁴Ammonium dichromate is very effective with NH_4NO_3 propellants but not with NH_4ClO_4 propellants. Fe_2O_3 and compounds giving rise to SiO_2 are very effective in increasing the burning rate of NH_4ClO_4 propellants but not that of NH_4NO_3 propellants.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

have often been achieved with NH_4ClO_4 propellants over practical pressure ranges. Very often, composites follow the law $r = a P^n$ very closely in the range 100 - 2000 psi. In many cases, however, it is necessary to apply the law to two or three separate regions in the pressure range mentioned.

The addition of metal powders to composite propellants in general does not drastically change the burning rate-pressure dependences outlined above. Aluminum and boron generally have small effects until the particle size of the powder is quite fine. For example, the decrease of aluminum particle size from 35 microns to 7 microns does show an increase in burning rate (Ref. 1). It has also been observed that the addition of small amounts of boron (2-5 wt %) lowers the pressure exponent (Ref. 5). Additional data on the comparison of aluminized propellant of varying aluminum contents are shown in Table V.

2. Double-base propellants. The mechanism of double-base-propellant burning differs considerably from that of composite-propellant burning and has been the subject of much investigation. Despite the considerable amount of work done with regard to double-base propellant-burning mechanisms, discovery of the dramatic effects caused by the addition of lead salts came as quite a surprise. In fact, the accidental discovery results from an attempt to improve the extrudability of double-base propellant. The so-called plateau and mesa effects are shown in Fig. 5. Curve B illustrates the plateaus where burning rate is independent of pressure in a certain region. Curve C illustrates the mesa effect. The entire effect is different from anything yet encountered with composite propellants. A typical $\log r$ vs $\log p$ plot for double-base propellants, as well as many composite propellants, is shown by curve A of Fig. 5. The effect of lead salt addition is shown schematically⁵ by curve C, and the shaded area under curve C represents the region of super-rate, which disappears as the pressure is increased, thus producing plateaus or mesas. In the pressure range where the burning rate decreases with

⁵A complete discussion of plateau and mesa formation and the catalysts producing the effects is beyond the scope of this presentation.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

pressure, the temperature-sensitivity is exceptionally low, as might be expected. Curve B is typical of composite propellants which have a tendency for plateau formation. A burning-rate catalyst for composite propellants causes loss of the plateau and a return to the dependence shown in curve A.

When the need arose for significant increases in performance of double-base propellants, the use of metal additive was considered. However, the double-base propellant ingredients do not have the excess oxygen required to burn the metals which are, in a sense, super-fuels. It was necessary to incorporate an oxidant, and again ammonium perchlorate was employed. It is perhaps not surprising to find, therefore, that such propellants do not exhibit the plateau and mesa effects and, in fact, have pressure exponents around 0.3, as reported recently by Allegany Ballistics Laboratory (Ref. 6).

B. Temperature sensitivity

To facilitate discussion, a few simple relations involving temperature sensitivity are given below:

$$\text{Basic definition} = \pi_K (\text{temperature sensitivity}) = \frac{1}{p_c} \left(\frac{\partial p_c}{\partial T_a} \right)_K \quad (1)$$

$$\pi_K = \left(\frac{1}{1-n} \right) \left(\frac{1}{r} \right) \left(\frac{\partial r}{\partial T_a} \right)_p = \left(\frac{1}{1-n} \right) \pi_p \quad (2)$$

$$\pi_K = \left(\frac{1}{1-n} \right) \left(\frac{1}{T_s - T_a} \right) \quad (3)$$

where

p_c = rocket-motor chamber pressure.

p = pressure in rocket-motor chamber or closed bomb.

$r = aP^n$, where $a \sim \left[1/(T_s - T_a) \right]$ for Eq. (3).

n = pressure exponent.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

T_a = uniform temperature of propellant grain prior to ignition, or ambient temperature.

T_s = surface temperature of solid propellant during steady-state combustion.⁶

The above relations give an indication of the various methods which are available for the reduction of temperature sensitivity.⁷ The methods will be illustrated by results of the Aerojet program⁷ devoted to the understanding and control of temperature sensitivity in solid propellants. Method I consists of adding decomposition catalysts such as $\text{CuO} \cdot \text{Fe}_2\text{O}_3$. There is a resulting increase in burning rate, increase in T_s and decrease in π_K . The only relation this might have to metal-powder addition is the effect noted when the particle size becomes very small and burning rates increase. Even if catalysis is not involved, the net result is the same on temperature sensitivity. Method II involves the addition of a metal in wire form, in which the metal has a negative temperature coefficient. In this regard, it should be mentioned that oriented wires can also reduce π_K by reducing n . Method III relates to the addition of any substance which drives the main decomposition reaction into the solid phase. The reduction resulting in n in turn reduces π_K . Aerojet has found that Isano oil produces this effect in polyurethane compositions. There does not appear to be any effect of this type with the metal additives known at present. Method IV involves the promotion of minor grain breakup below the burning

⁶The assumption of T_s is part of a successful empirical formalism which has proved convenient in qualitative discussion of the factors affecting propellant-burning, as exemplified by the present discussion. More fundamental treatments of the factors relating to temperature sensitivity have been made, but in light of the present knowledge of solid-propellant burning mechanism do not yield much additional qualitative information over the present simplified empirical discussion.

⁷The author is indebted to Dr. E. Mishuck, Mr. A. J. Secchi, Mr. D. A. Seedman, and their collaborators for the opportunity to discuss the results of an extensive study of temperature sensitivity which they are conducting under Navy BuOrd sponsorship. Generalities evolved in their investigations are used in the present discussion. During the course of this work, a Handbook of Temperature Sensitivity Data is being prepared for general use in the propellant field.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

surface, owing to the presence of an additive which decomposes thermally and gives off gaseous products. Aerojet cited the use of CaC_2O_4 and CaCO_3 . The effect is the same as that resulting when the controlling reactions are made to occur in the solid phase. It is likely that effects of this type will be observed with metal hydrides when sufficient data are available. Method V involves the production of a heat sink, and magnesium is cited as an example by the Aerojet group. Undoubtedly, this is a major reason for the effectiveness of boron in reducing π_K , and many other metals and alloys can also be expected to have similar effects.

The complexities of the π_K problem relating to metal additives are also beautifully illustrated by work at Aerojet in which it was shown that heat treatment of Al produced aluminum in such a form that lower π_K 's resulted when it was introduced into propellant compositions.

C. Wires versus powders

There are several ways in which metals can be added to propellants, and certain methods of addition have more effect on the combustion characteristics of the solid propellant than others. Up to this point in the presentation, uniform dispersion of fine metallic powders throughout the propellant composition was primarily considered. It has been shown that adding metals in this manner usually causes relatively small changes in combustion characteristics. The addition of metals in the form of wires oriented perpendicular to the burning surface has been used in an ingenious manner by the Atlantic Research Corporation to provide large over-all changes in solid propellant combustion (Refs. 7, 8, 9). Before discussing certain aspects of the burning of propellant containing long continuous wires oriented parallel to the burning surface, a few remarks will be made concerning other forms of wire addition. In one instance, an attempt was made to add chopped iron wire to a propellant mix and then orient the wire before curing with a magnetic field (Ref. 10). Results of the experiment were erratic, and the change in burning rate was relatively small. The addition of tin wire has already been mentioned in Sec. III-B in connection with lowering the temperature sensitivity.

The use of wire in continuous form, embedded in a propellant matrix, effects a considerable enhancement of the mass burning rate. This increase in rate is essentially due to a change in the quantity of the burning surface. The result is a controlled worm-holing of the charge (Ref. 7). The effect is generally greater, at high pressures, for metals of greater thermal diffusivity, except for those whose

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

melting points lie near the propellant surface temperature. Little effect is noted at low pressures. When the burning rate of the matrix is of the order of 0.06 in./sec, an effective increase in the pressure exponent occurs. The increase is often earlier for wires of greater diameter. When the ratio of the apparent to the linear burning rate is of the order of 3 to 5, the pressure exponent returns to a value near that of the matrix for many metals. The apparent rate then roughly parallels the linear burning rate. In this region, wires of larger diameter generally yield lower pressure exponents (Ref. 8). Short segments of wire yield similar effects. Also, efficiency of the wire decreases with increasing wt % of metal (Ref. 9).

Simple thermal and geometric arguments,⁸ assuming no effect of the wire on the linear burning rate of the matrix, predict qualitatively the sigmoid curves obtained for burning rate along the wire. For non-melting wires, it also predicts rather accurately the dependence of the apparent burning rate at high pressures on the square root of the thermal diffusivity of the metal of homogeneous wires. The dependence on wire diameter in the region of large pressure exponent is also qualitatively satisfied, even though the relation was derived for thin, wide metallic ribbons. The mathematical relationship which was derived is as follows:

$$\frac{r}{r_p} = \left\{ \frac{\frac{\kappa}{\kappa p} - \frac{1}{2} \left[\phi(r_p) \right]^2 - \sqrt{\frac{1}{4} \phi^4 + \frac{\kappa}{\kappa p} \left(\frac{\kappa}{\kappa p} - 1 \right) \phi^2}}{1 - \phi^2} \right\}^{1/2}$$
$$\phi = \frac{2k_p}{c \rho l r_p}$$

⁸The present simplified treatment of the effect of oriented wires on propellant burning is part of general study of this subject conducted by P. C. Hanzel and the author. It is intended that a more systematic treatment of the subject be presented as a separate publication. The Atlantic Research Corporation reports also analyze by independent methods the general problem of the burning of propellant along wires and demonstrate the importance of heat conduction along the wire in causing the observed effects.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

where

r = apparent rate.

r_p = linear burning rate.

κ = thermal diffusivity

c = heat capacity.

l = ribbon thickness.

ρ = density.

k = thermal conductivity.

p = reference to propellant.

D. Unstable burning

There is a considerable amount of evidence which has shown that the addition of small amounts of metals, such as aluminum, when introduced into a propellant composition reduces, and in most cases entirely eliminates, the unstable burning conditions often encountered in rocket-motor firings. Experience has shown that the amount of metal usually required is in the vicinity of 2% by weight of the over-all propellant composition. Of course, the addition of more metal than this would still retain the beneficial effect of removing unstable burning. It is somewhat fortuitous, therefore, that in order to get increased performance in the rocket propellant, it is necessary to add metal, which also has the beneficial effect of removing this undesired instability in burning. It is, of course, important to understand the manner in which the metal powder tends to remove the unstable burning condition, and it would be desirable to know whether or not chemical kinetic effects, heat transfer effects, and other associated phenomena play a part in damping out the oscillations which are detrimental to the motor behavior. One should proceed at the present time, however, with a great deal of caution, particularly with respect to applying chemical kinetics or chemical interpretations to the reduction of unstable burning tendency. For example, it has been observed that the combustion products, such as aluminum oxide, are quite effective in reducing unstable burning and, on a weight percentage basis, probably have roughly equal effectiveness. Also, it appears that particle size has an effect on the additive on the reduction of

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

unstable burning; but again, this is not something which appears to be unique with respect to the metal or to the essentially chemically inactive oxides. As a matter of fact the entire effect relating to the reduction of unstable burning might be a result of physical rather than chemical factors. The possibility has been suggested that the solid particles have a damping effect on the acoustical oscillations which are present in the motor. The mechanism of initiating these oscillations, and a full definition of all the conditions under which unstable burning can occur, is not clearly known or well defined at this stage of our knowledge, and there is much active work still going on in the field.

E. Ignitibility, shock sensitivity and detonability

The properties of ignitibility and shock sensitivity are in some ways closely related; however, the interest in each takes on different aspects when related to practical application. For example, most propellant compositions are relatively easily ignited at room temperature and above. It is only ignition at low temperature which usually causes concern among different formulations. Also, the problem of ignitibility after long-term storage is important. However, this problem is usually associated with surface effects, and to this extent ignitibility and shock sensitivity are quite unrelated. The addition of metal powders can have both good and bad effects on shock sensitivity. Particle shape, hardness, and melting point of the metal or alloy are contributing factors in altering shock sensitivity. No special problems have been encountered in the ignitibility of metallized propellants.

A subject even less understood is that of the conditions under which metallized solid propellants undergo transition from steady-state deflagration to detonation. Experimental results on various propellant types containing metals do not show any appreciable increase toward detonation, with the exception of those compositions of a very high solids content and thermally sensitive binders. No really systematic and definitive data are available in any event. Aerojet has claimed that certain of the Polaris propellants with ammonium perchlorate, aluminum, and low-energy polyurethane binders have the properties of Class B explosives at ambient temperatures, according to ICC classifications (Ref. 1).

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

IV. MOTOR PERFORMANCE

A brief discussion of motor performance will be given for the purpose of illustrating the general effects of metal additives on performance.⁹

A. Propellants containing aluminum

Practically all large rocket-motor development employing metallized propellants has been restricted to the use of aluminum powder up to now. Thiokol has fired large motors containing aluminized ammonium perchlorate-polybutadiene acrylic acid propellant. The specific impulses of all the large motor firings using the PBAA-type propellant are usually in the 240 - 245 sec. range.¹⁰

Aerojet reports¹¹ specific impulses in the range of 240 to 252 for aluminized polyurethane propellants containing low-energy polyurethane binders. In this connection, it was called to the author's attention by Drs. A. Dekker and C. Rogers that significant differences in performance were encountered with 3KS-1000 motors containing 15 - 20 lb of propellant and 10KS-2500 motors containing 90 - 100 lb of propellant as the aluminum content of the propellant was increased. The larger motors consistently gave higher results and the specific impulse would, in general, level off at some maximum value once the metal content approached 20 - 22 wt % aluminum, whereas the smaller motors tended to show a maximum specific impulse at metal contents of around 15 - 17%. It was the combined opinion of Dr. Dekker and his collaborators that the 90 - 100 lb motors were about the smallest motors which gave results useful for further scaling to arbitrarily larger sizes.

⁹The author is indebted to John Coy for reviewing work in this field, and particularly for making available results of his investigations at the Jet Propulsion Laboratory.

¹⁰A sea-level specific impulse at 1000 psi chamber pressure is used throughout this paper.

¹¹Results of work performed at Aerojet under Contract No. AF 33(600)-36610.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

As the energy content of the resin binders of the aluminized propellant was further increased, for example through the addition of nitro and nitric ester plasticizers to the polyurethane binder, the use of other high energy binders, such as polyurethanes based on nitro-polymers, and the use of acrylic binders such as petrin acrylate and double-base binders, all gave the maximum specific impulses in the 250 - 260 sec range. Thus, there seems to be little question that high-energy and thermally sensitive binders lead to maximum combustion efficiency and performance for aluminized propellants. Motor data are also available which demonstrate the following effects clearly:

1. Catalysts increasing the burning rate of the propellant produce increased combustion efficiency.
2. Reduction of the particle size of aluminum increased combustion efficiency.
3. Any factors substantially increasing the burning rate of the propellant time increased combustion efficiency.

B. Miscellaneous results

Although most of the work on alloys of magnesium-aluminum is only preliminary, several agencies have strong indications that combustion efficiencies are improved, as indicated by motor data. Tests have been made at JPL with magnesium hydride, zirconium hydride, and other materials, but none of the data are sufficiently reliable to report at this time. It is to be expected that considerable amounts of data will become available in these areas within the next year. Boron has consistently given low results with respect to combustion efficiency in motor tests; however, very little work has been done with this additive. There has been much discussion of the possibility of using beryllium to increase performance, and again no actual motor tests have been conducted. It obviously will be very difficult to conduct tests of this type because of the high toxicity associated with beryllium components. Also, it would be desirable at an early date to have a few definitive motor tests to be conducted on propellant systems containing boron hydrides, such as decaborane. Such data would be particularly valuable in comparing the combustion efficiencies of the hydrides with those of amorphous boron.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

C. Problem areas

In the preceding Sections on motor performance, it has been shown that the problem of increasing combustion efficiency in burning metal powders in propellant compositions is a very important one, and one which should be studied in every possible detail. In this manner, one might not only optimize and maximize a motor performance for a given metallized system, but it may be possible in some instances to utilize a metal powder and get high combustion efficiency where otherwise one might find the metal powder of little use in increasing performance, simply because it could not be made to burn properly. A more quantitative understanding of the relationship between motor size and combustion efficiency of the metal powder is particularly needed.

We have mentioned essentially all of the problems up to now concerned with modification of combustion characteristics of propellants and also the stability problems encountered in introducing metal powders into propellants. There are, however, additional problem areas in the use of metal powders in increasing motor performance, and probably the most important one has to do with the study of motor performance when expanding into a relatively good vacuum. Also, there needs to be much more work done on the effect of area ratio and nozzle contour in obtaining the highest and the most complete combustion efficiency. Another problem area is that of the expansion processes and the tendency or degree of approach of equilibrium of the various chemical species which are exhausted in the nozzle. This is particularly important in optimizing performance over a wide variety of expansion ratios and expansion into varying degrees of vacuum. There is, of course, the additional problem of knowing not only whether the particles being exhausted are formed in times comparable with the residence time in the motor nozzle and exhaust section, but also as to whether the particles go along with the stream. Considering all the complex metal systems which might find application in the next few years, there certainly are a great number of problems in these areas which should be given close attention. It might also be mentioned that in connection with thrust control and thrust termination, the properties of metallized systems should be defined very carefully with respect to properties, such as flame stability and extinction at low pressure.

Finally, it should be mentioned that the well-known problem of erosive burning still needs further investigation, particularly with respect to the comparison of metallized and non-metallized systems containing wide variations in metal content. Up to now, there is little

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

information along these lines which is sufficiently detailed to clarify either quantitatively or qualitatively, the general nature of the effect of metal additives on the erosive characteristics of some of the presently used propellant systems.

V. SUMMARY

More important aspects of the effect of the addition of metal additives to solid propellants on combustion and performance are summarized below.

A. Metal additives have been successfully used to produce significant increases in the performance of present-day solid propellants. An important factor in achieving the maximum performance increase concerns the extent of combustion of the metal powder before it leaves the rocket-motor exhaust. The many aspects of metal powder combustion in solid propellants have added greatly to the complexity of solid-propellant development, and much additional information along these lines will be needed in the near future.

B. The most used metal in present-day compositions is aluminum. Combustion efficiencies of aluminized propellants have been particularly low in small motor tests (85 - 90%) and have greatly reduced the value of many preliminary tests in the evaluation of these systems. Even though it has been observed that combustion efficiencies level off as motor size is increased, the scaling laws are inadequately understood.

C. Difficulty has been encountered in obtaining high combustion efficiency of boron in propellant compositions.

D. Alloys of metals, such as magnesium-aluminum alloys, have shown promise in increasing combustion efficiency where the pure metal offers difficulty.

E. Another important factor in increasing combustion efficiency is that of increasing the oxygen content and combustibility of the resin binder. Highly nitrated resin binders in general give far greater combustion efficiencies for a given size motor than essentially non-oxygen containing binders, such as butadiene copolymers.

F. General combustion characteristics of the propellant composition, such as burning rates, pressure exponents, and

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

temperature sensitivities, are affected by the addition of metal additives; however, the effects are generally not large, and care is required in obtaining reproducible and definitive results.

G. The effect of particle size of the metal additive is usually not very effective in increasing combustion efficiency until the particles become very small, of the order of microns or less.

H. The addition of metals in the form of oriented wires causes far greater change in over-all burning characteristics than does the introduction of metal powders into solid propellants. The use of oriented wires, however, will probably be of no great value in increasing the performance of solid propellants but will merely serve as a technique of achieving high burning rates for special application.

I. Miscellaneous aspects of the metal additive effects on solid propellants are as follows:

1. Metal powders in quantities of 1 or 2% or greater substantially reduce unstable burning in solid rocket motors.
2. Shock sensitivity, ignitibility, and detonability are areas in which effects are not clearly understood and defined at present. However, there is no reason to expect adverse effects in these areas.
3. Additional work is required in understanding the physical and chemical aspects of the expansion process, particularly when expanding into a vacuum.
4. Much is needed in the way of understanding the more detailed burning mechanism of composite propellants containing metal additives.
5. It is generally desirable to look quickly at the combustion-efficiency problem once a given additive shows promise of an over-all appreciable increase in performance; beryllium metal serves as an example.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

Table I. Ease of Particle Ignition¹

Relatively Easy	Relatively Difficult
Mg, MgH ₂ , Ti, TiH ₂ , TiC, Zr, ZrH ₂ , ZrN, CaH ₂ , LiH, LiAlH ₄ , Sb, Fe	Al, TiAl ₃ , B, Si, TiB ₂

¹Relative ease of ignition of particles of size range -325 mesh (-44 microns) using particle burning torch. The group of easily ignitable substances includes all of the rapidly burning substances, but also two slow-burning substances, Sb and Fe.

Table II. Ignitibility Limit¹

Substance	Particle Greater Than
Al	150 microns
Mg	250 microns
Ti	> 420 microns
CaH ₂	> 420 microns
LiAlH ₄	> 420 microns

¹Largest particle size ignitable with particle-burning torch by pilot flame of any size.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

Table III. Degree of Boron Combustion
in Polyurethane Propellants

Sample No.	Nominal B Content	Sample Weight	% B Oxidized	% B Un-Oxidized
X550B-75-5B ¹	5%	4.226	59.5	40.5
		4.576	<u>50.1</u>	<u>49.9</u>
			avg 54.8	avg 45.2
X500B-80-10B	10%	3.345	40.9	59.1
		3.561	<u>38.3</u>	<u>61.7</u>
			avg 39.6	avg 60.4
X550B-72.9-5B	5%	4.428	55.0	45.0
		4.549	<u>60.6</u>	<u>39.4</u>
			avg 57.8	avg 42.2

¹The composition of JPL X550 is as follows:

Polyurethane resin containing:

polypropylene glycol 2025	80.0%
1, 2, 6 hexane triol	4.0%
toluene diisocyanate	16.0%

Fuel binder containing:

polyurethane resin	75.0%
Triton-100 (wetting agent)	5.0%
trimethylene glycol dinitrate	20.0%

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

Table IV: Effect of Tube Length on Extent of Boron Combustion

Length	Aspect Ratio	B Oxidized, gm
11 in.	16	0.11
3 in.	4.7	0.11
1 in.	0.45	0.085

Table V. Burning-Rate of Aluminized JPL X550 Propellant

% NH_4ClO_4	% Al	Aluminum Particle Size microns	Burning Rate in. /sec at 1000 psi
80	0	-	0.34
70	10	5	0.44
65	15	35	0.42
65	15	5	0.46
70	15	5	0.55
85	0	-	0.42

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

REFERENCES

1. Polaris Power Plant Development, (Period covered: December 1958), Report No. 3520-01M-15 Aerojet-General Corporation, Azusa, California, January 20, 1959 (Confidential).
2. Flourney, J. M., and Klotz, M. A., Research, Development and Rocket-Motor-Evaluation Testing of Nitropolymer Propellants, (Period covered: July 16 - October 15, 1957), Report No. 2795-2(Quarterly). Aerojet-General Corporation, Azusa, California, November 15, 1957 (Confidential).
3. Bulletin of the Seventh Meeting of the JANAF Solid Propellant Rocket Static Test Panel, Bulletin NOrd-7386. Johns Hopkins University Applied Physics Laboratory, October 1958 (Confidential).
4. Stosick, A. J., "The Ballistic Improvement of Ammonium Nitrate Propellants," Addendum to the Bulletin of the Tenth Meeting, JANAF Solid Propellant Information Agency, p. 55, June 1954.
5. Nichols, P. L. Jr., Reger, Jo L., and Hanzel, Paul C., High Performance Polyurethane Propellants, Publication No. 60. Jet Propulsion Laboratory, Pasadena, California, January 1956, (Confidential).
6. Formulation Studies of Very High Impulse Propellants, Report P-40. Allegheny Ballistics Laboratory, January 1959 (Confidential).
7. Research and Development Programs in Fields of Solid Propellants and Interior Ballistics (Period covered: July - September, 1954) Quarterly Progress Report No. 18. Atlantic Research Corporation, Alexandria, Virginia, January 1955.
8. Research and Development Programs in Fields of Solid Propellants and Interior Ballistics (Period covered: October - December 1954), Quarterly Progress Report No. 19. Atlantic Research Corporation, Alexandria, Virginia, April 1955.

~~CONFIDENTIAL~~

~~CONFIDENTIAL~~

REFERENCES (Cont'd)

9. Research and Development Programs in Fields of Solid Propellants and Interior Ballistics (Period covered: January - March 1955), Quarterly Progress Report No. 20. Atlantic Research Corporation, Alexandria, Virginia, September 1955.
10. Combined Bimonthly Summary No. 51 (December 1, 1955 to February 1, 1956). Jet Propulsion Laboratory, Pasadena, California, (Confidential).

~~CONFIDENTIAL~~

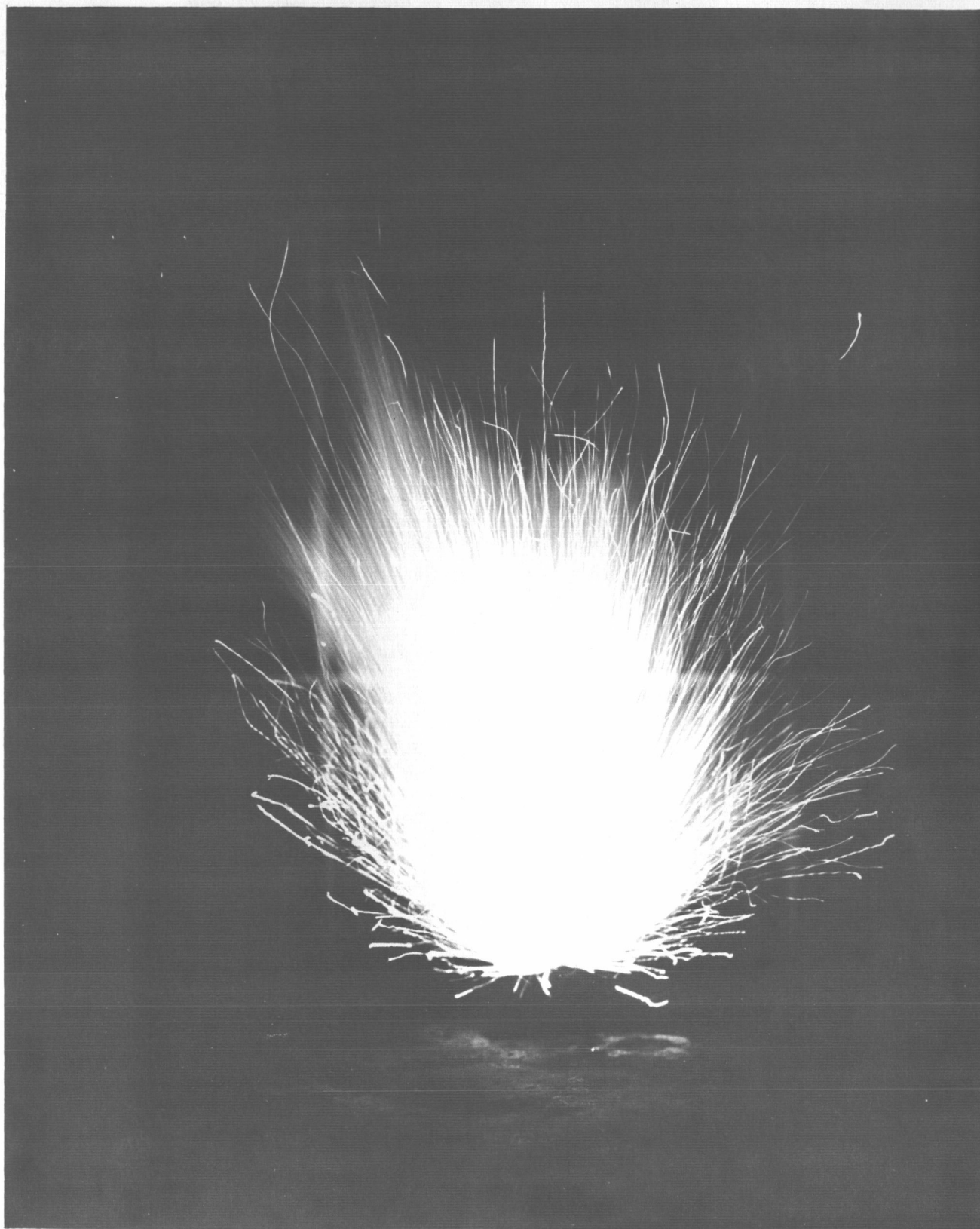


Fig. 1. Aluminized Propellant Burning

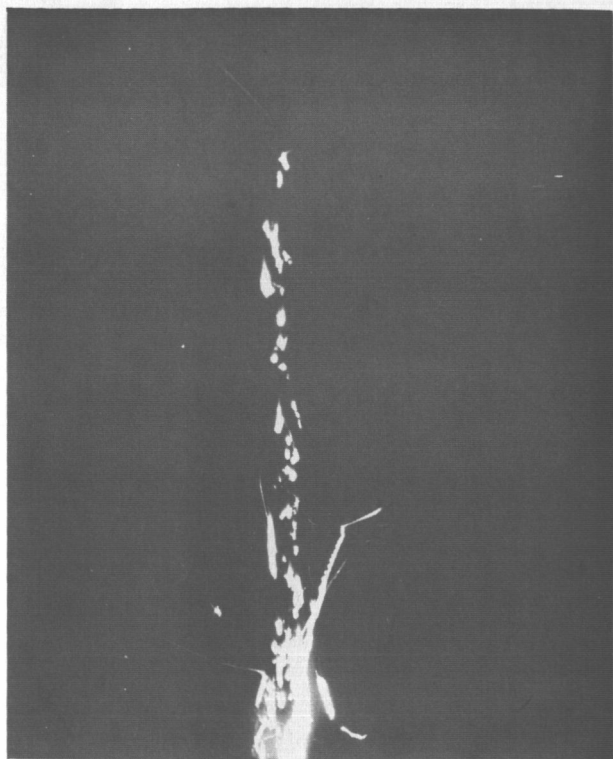


Fig. 2a. Mg Particles Burning in Pilot Flame

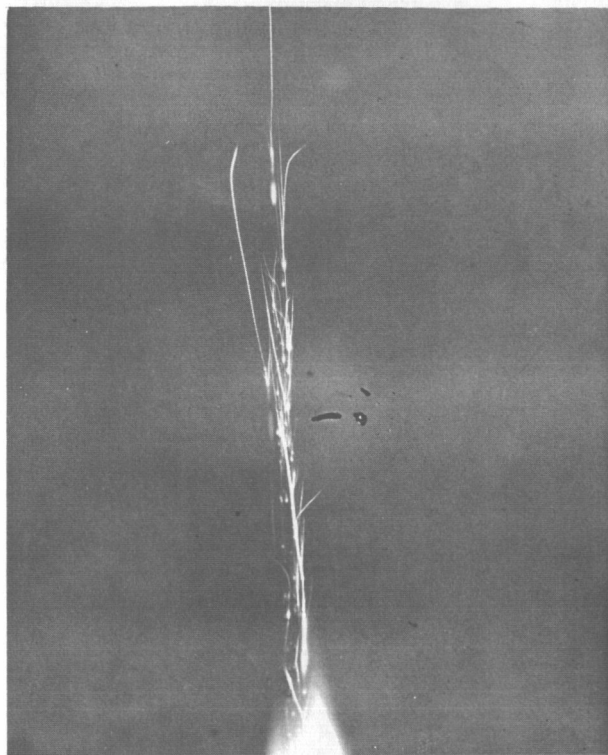


Fig. 2b. LiAlH_4 Particles Burning in Pilot Flame



Fig. 2c. Al - Mg (75-25 wt %) Particles Burning in Pilot Flame



Fig. 2d. Ti Particles Burning in Pilot Flame

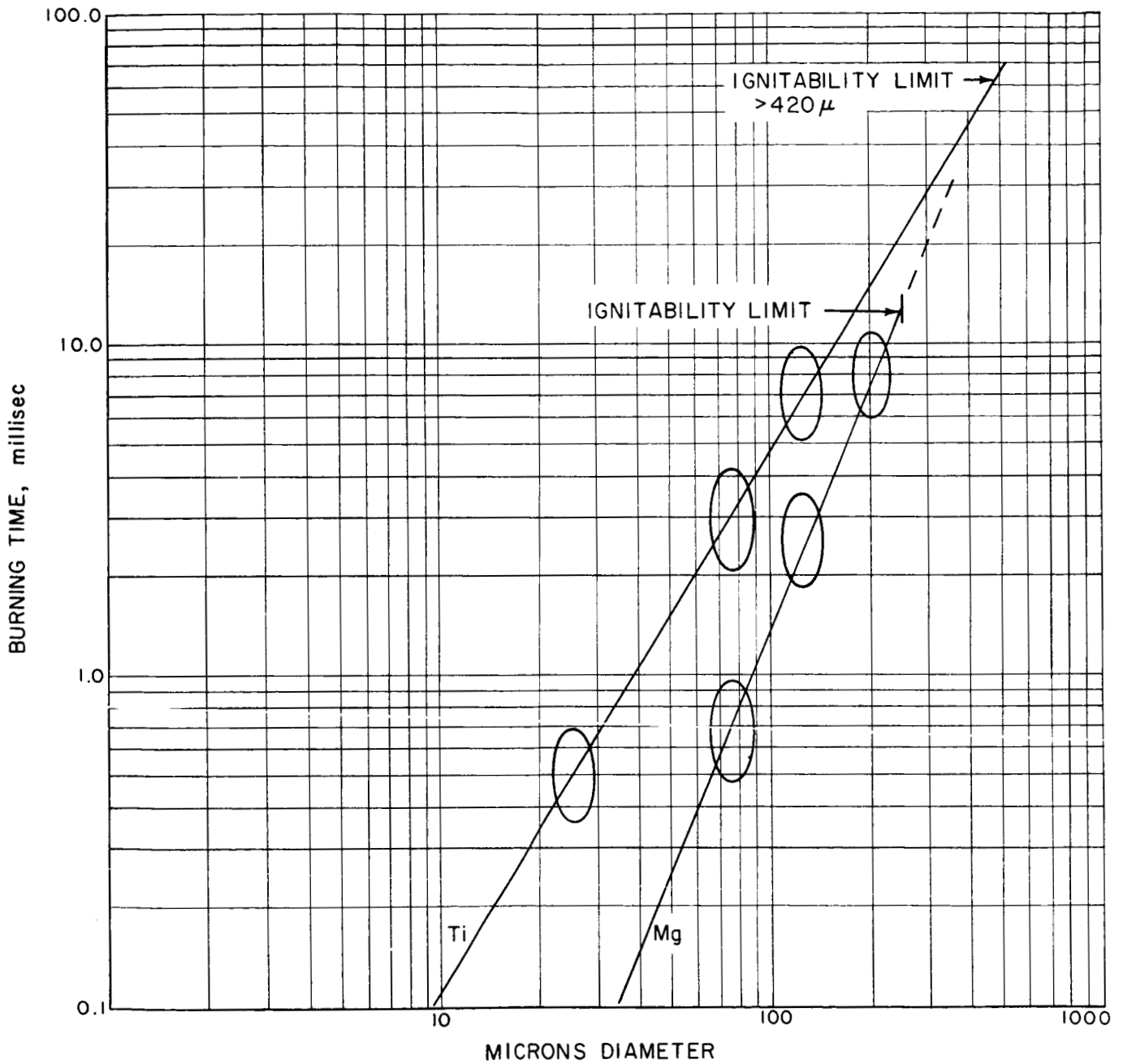


Fig. 3. Burning Time vs Diameter for Mg and Ti Particles

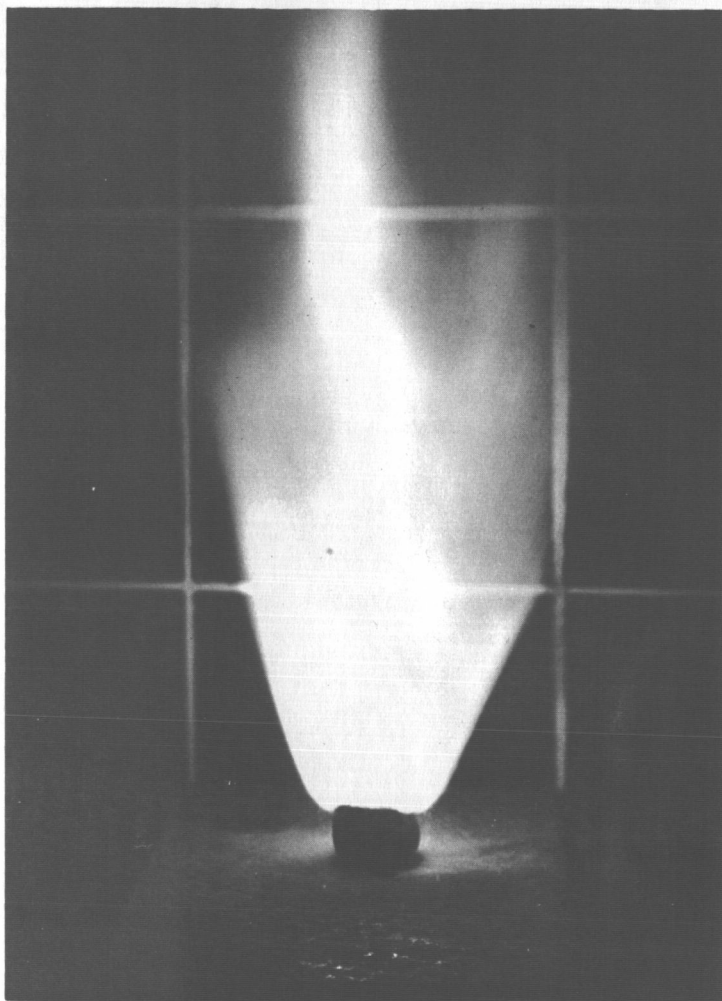
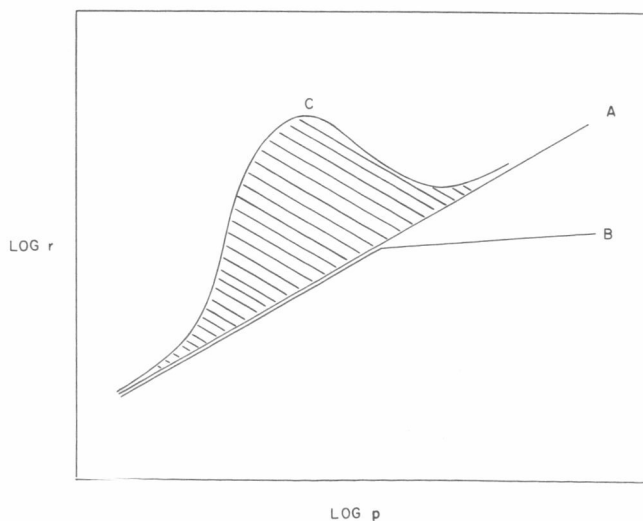


Fig. 4. Burning of Propellant
Containing Mg - Al
(50-50 wt %) Alloy

Fig. 5. Generalized Burning-Rate
Curves



LOG p